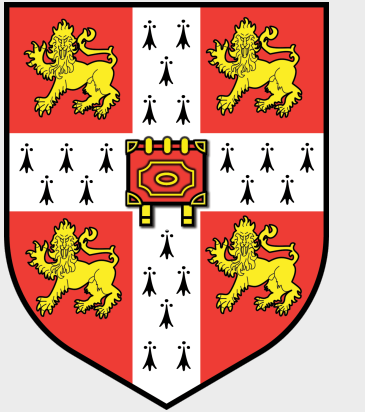


The Derivative Discontinuity from H₂ to the Anderson model

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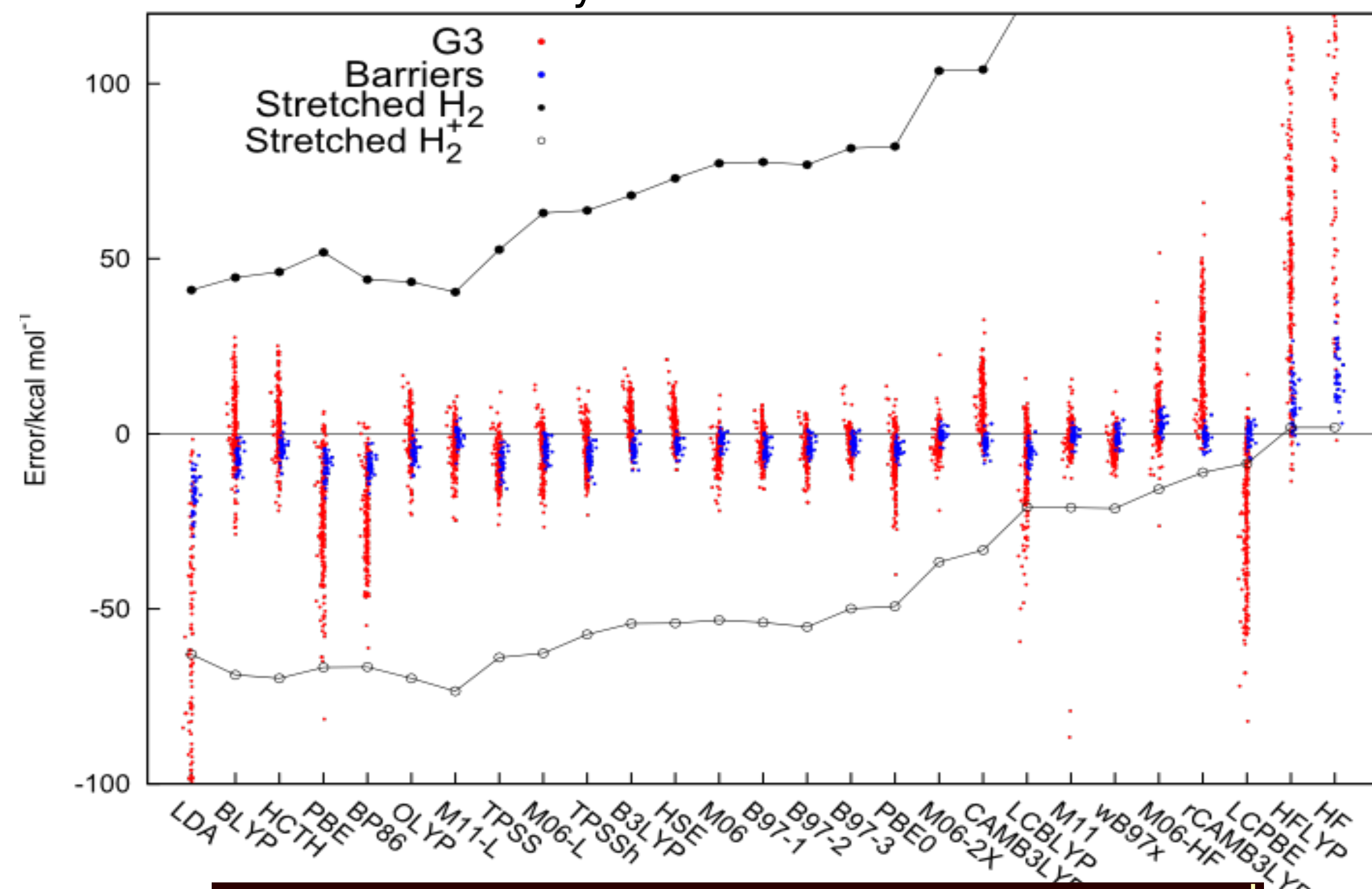
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Exchange-Correlation Functionals

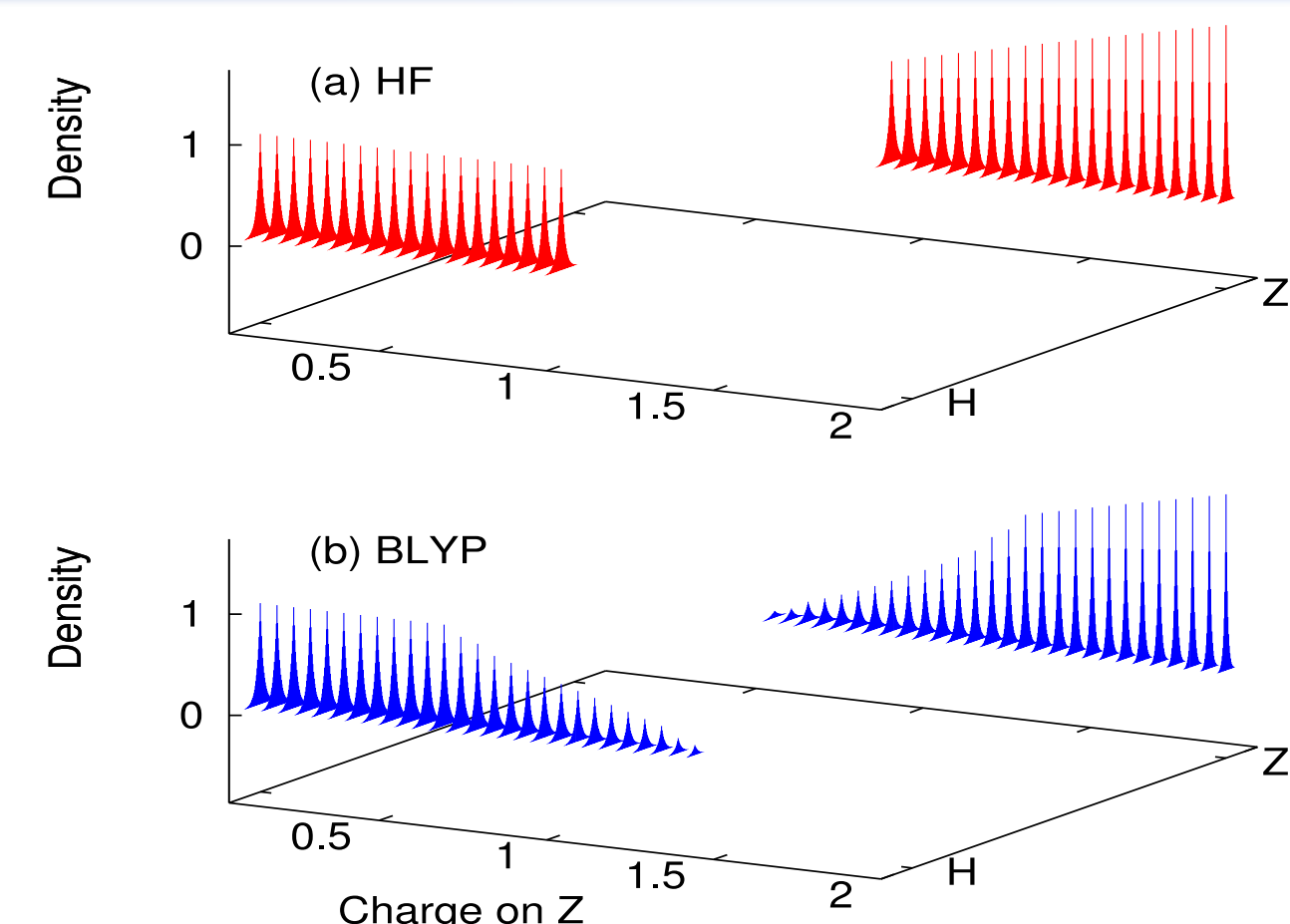
Here we show the performance of many different exchange-correlation functionals. Individual errors are shown for all the molecules in the G3 set as well as a standard set of Hydrogen-transfer barriers. The errors for infinitely stretched H₂⁺ and H₂ are massive. This error is a manifestation of the derivative discontinuity.



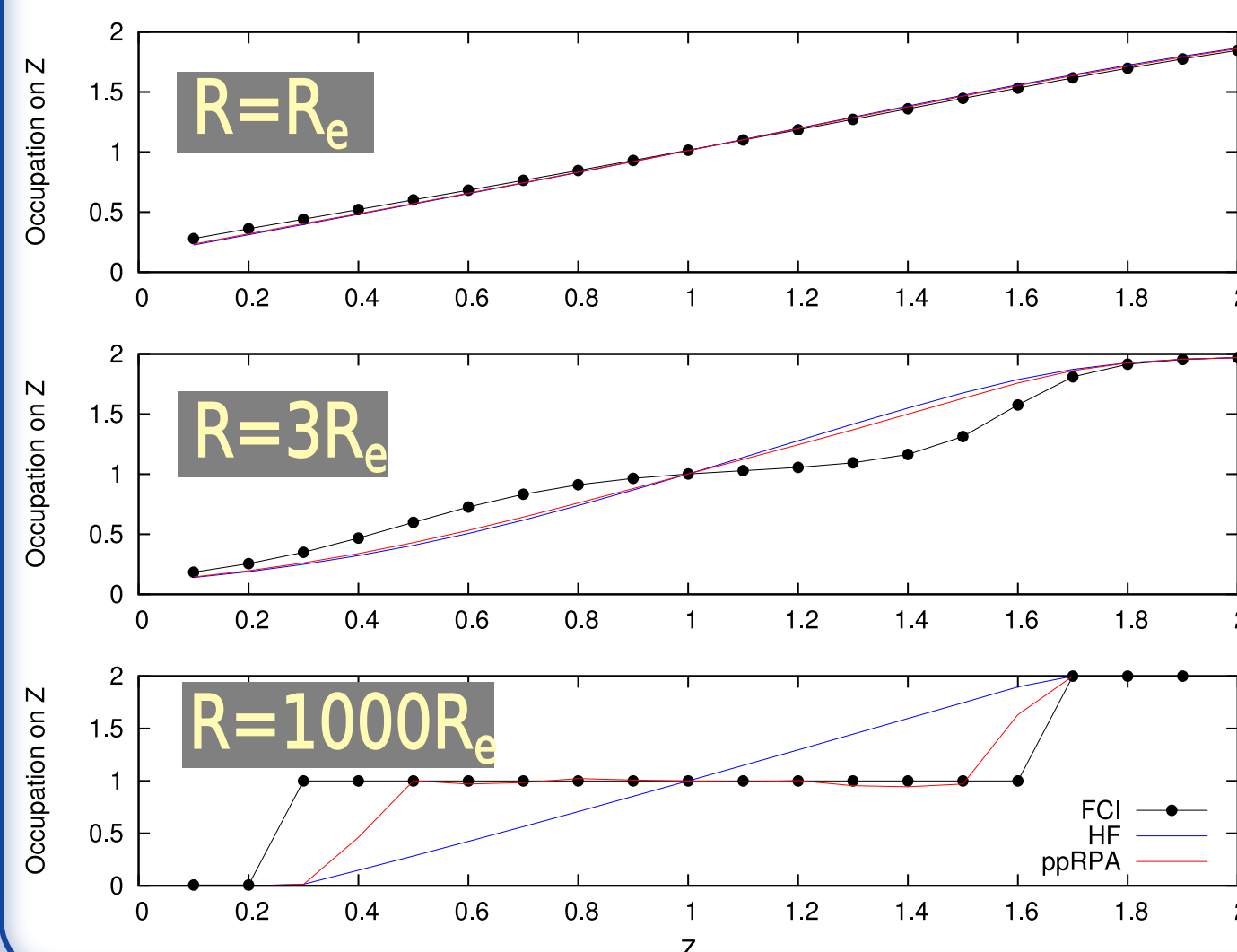
Performance of functionals including failure for H₂/H₂⁺

Fractional Nuclei: a tool for theoreticians

We have seen that the energy of two protons with one and two electrons is a massive challenge for all DFT methods. What about the density? Of course there is no problem as the density is constrained by symmetry. Now consider removing that symmetry by smoothly changing the nuclear charge on one of the protons. This is the HZ^{1e} molecule, HF is exact. At infinite separation we can see discontinuous behaviour of the density, and also the delocalisation error of BLYP.



The density of stretched HZ^{1e}

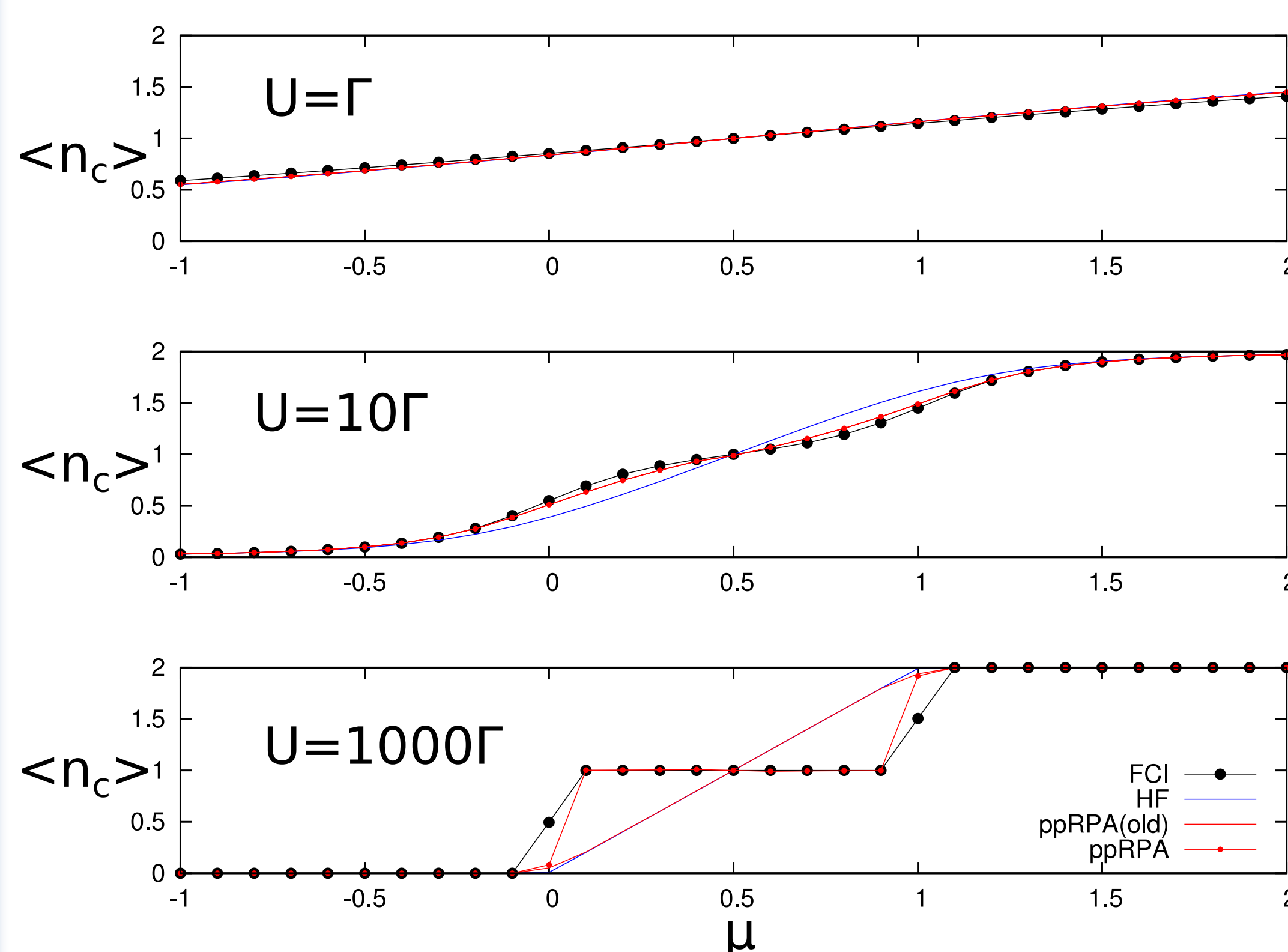


Now consider the same molecule but with two electrons, HZ^{2e}. Here we see the occupation of the density on the Z atom as a function of Z at three different bond-lengths. Very smooth behaviour is seen at equilibrium bond-length but as the distance is increased the FCI behaviour becomes very discontinuous exactly as in HZ^{1e}. Restricted HF completely fails to recover this behaviour.

The occupation of Z of HZ^{2e}: varying R

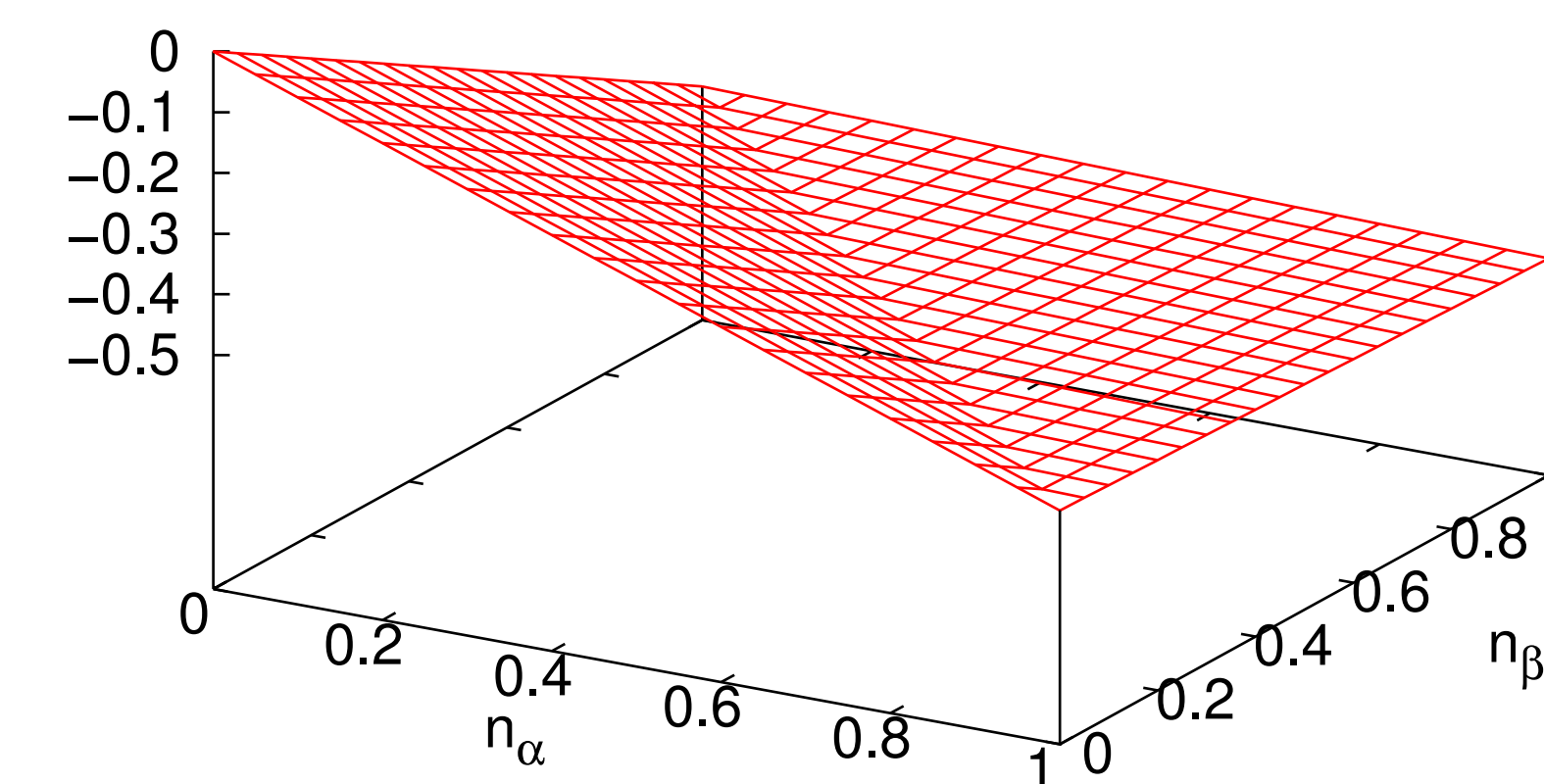
Anderson Model: occupation of the impurity site

We consider an Anderson model with several non-interacting sites with one impurity which has an electron-electron interaction term U compared to the hopping term Γ and an onsite chemical potential, μ . As we vary the chemical potential we can see the occupation of the impurity site change. This change in the large U limit is very discontinuous.

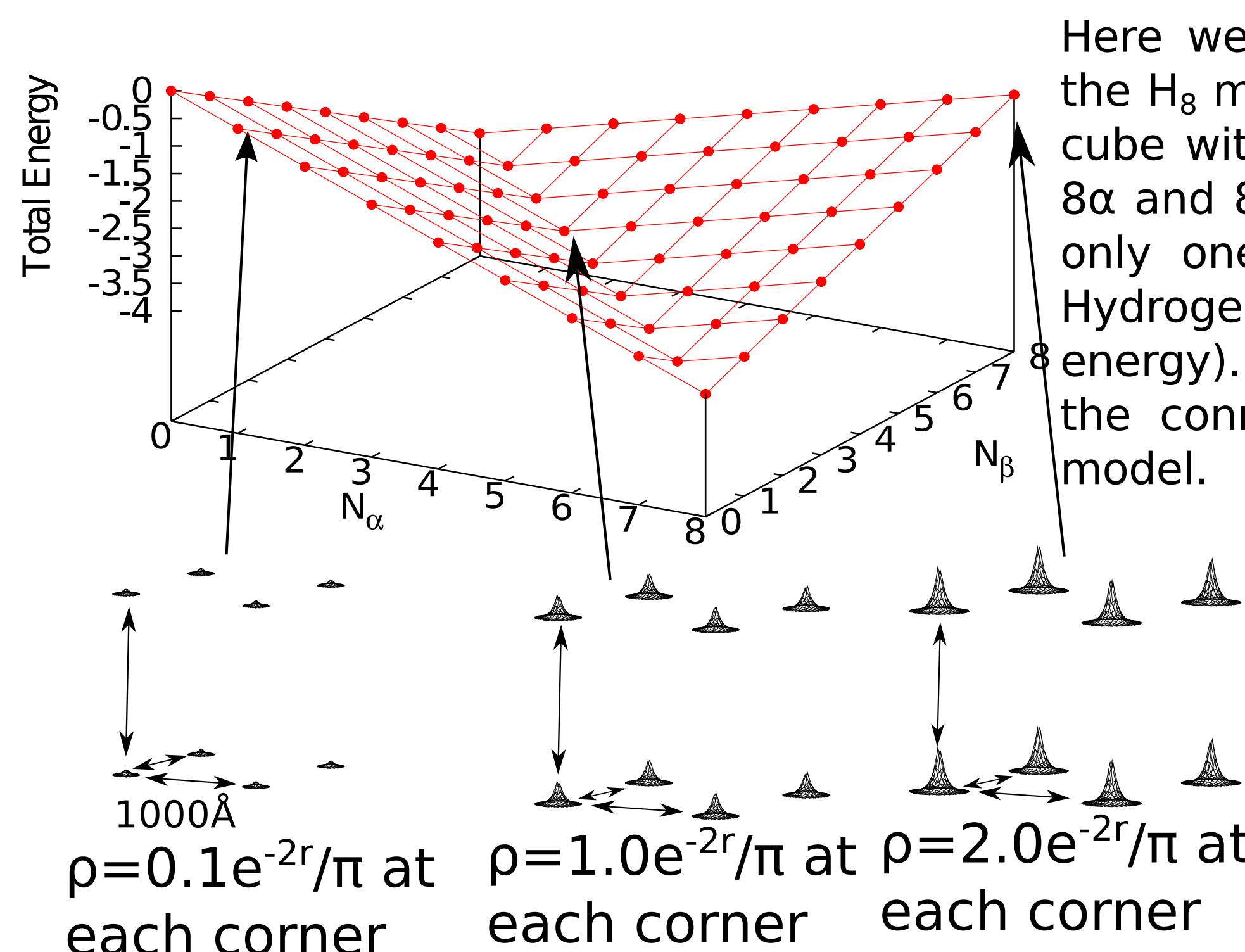


As has been shown by several authors the derivative discontinuity can be seen both in the transmission and the occupation on the impurity site. For example Stefanucci and Kurth PRL (2011). Evers and Schmitteckert PCCP (2011). Bergfield, Liu, Burke and Stafford PRL (2012).

Flat plane with integer numbers of electrons



Flat plane condition for fractional charges and fractional spins of one single Hydrogen atom from 0 electrons up to 1α and 1β electron. Exactly the same will be found for infinitely stretched Hydrogen clusters with integer numbers of electrons.



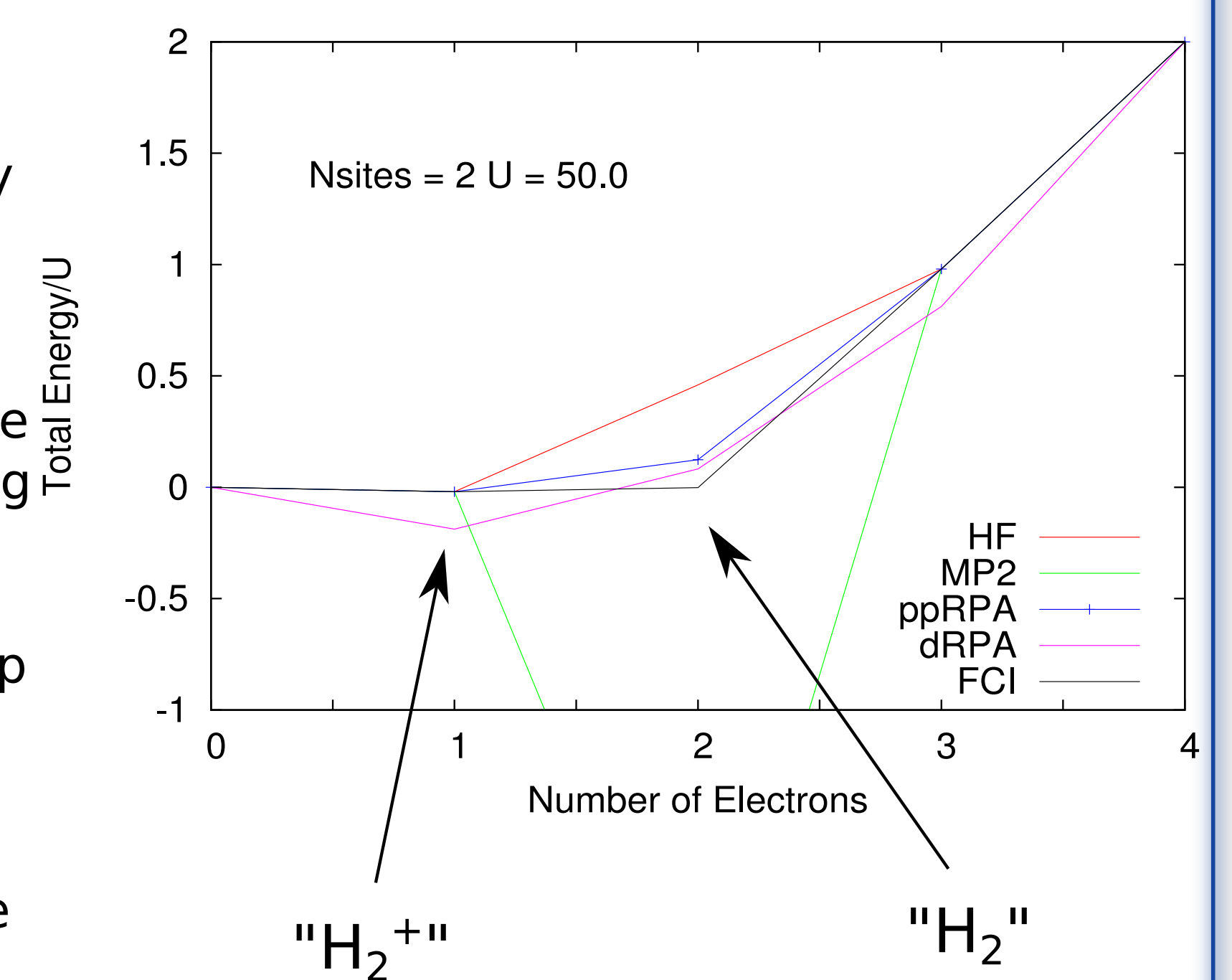
Here we have FCI calculations on the H₈ molecule at the corners of a cube with 0 to 16 electrons, up to 8α and 8β electrons. Also we have only one basis function for each Hydrogen (hence the rise in the energy). This is also to illustrate the connection with the Hubbard model.

With one basis function per Hydrogen and obeying the symmetry, the density change is completely smooth as a function of number of electrons. It shows no discontinuity on passing through 8 electrons (one electron per site).

However the FCI energy is very discontinuous, this is not captured by any current approximate functionals except for the very recent ppRPA of van Aggelen, Yang and Yang.

The gap of the 1D-Hubbard model

The 1D-Hubbard model contains the interesting physics of strong correlation. If we first consider the 2 site Hubbard model with occupation from 0 to 4. Of course the $U/t \rightarrow \infty$ limit corresponds exactly to infinitely stretched Hydrogen systems. In the following $t=1$. We investigate the large U limit to see how many-body methods perform. The Hubbard model nicely encapsulates the need to describe both H₂ and H₂⁺ with the same method to correctly describe the gap at half-filling (2 electrons). Here the recent ppRPA method from Yang and coworkers which has been shown to give the flat-plane also begins to correctly describe the gap of the 2-site Hubbard model. It is correct in the $U/t \rightarrow \infty$ limit. We can see the failure of methods such as MP2 which diverges for degenerate situations such as H₂ and dRPA which corrects that error but only at the cost of an error in H₂⁺.



However as the number of sites increases the gap from all many-body methods disappears. Here we can see in comparison to FCI that the gap $E_{\text{gap}} = E(15) + E(13) - 2E(14)$ from all approximate many-body methods are becoming smooth at half-filling. As we increase to more sites the gap gets even smaller even though the FCI is very close to the exact Bethe-Ansatz limit.

References

- H. van Aggelen Y. Yang and W. Yang, Exchange-Correlation Energy from Pairing Matrix Fluctuation and the Particle-Particle Random Phase Approximation, arXiv:1306.4957 (2013)
- A. J. Cohen, P. Mori-Sánchez and W. Yang, Challenges for Density Functional Theory, Chem. Rev. **112**, 289 (2012)